Surface vacancies in II–VI and III–V zinc blende semiconductors[a)]

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We present calculations of the bound state energy levels of ideal vacancies near the (110) surface of some zinc blende II–VI and III–V semiconductors: CdTe, ZnTe, GaAs, AlAs, InAs, and some alloys among them. Here we compare vacancies near the surface of II–VI's with those of III–V's. In contrast to the III–V's, where a neutral vacancy has an odd number of electrons, a neutral vacancy in a II–VI semiconductor has an even number. We find that single anion vacancies in III–V's can behave as both donors and acceptors, and follow observed trends with ionicity and alloy composition. We also find that single cation vacancies in II–VI's behave as double acceptors and the anion vacancies behave as shallow double donors. We suggest experiments to test the importance of vacancies in determining the Fermi level pinning position for II–VI's.

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I. INTRODUCTION

The recently proposed "defect model" of Schottky barrier formation[1] has had success in accounting for the observed behavior of Schottky barrier heights in III–V semiconductors. In this model it is proposed that defects created in the semiconductor during formation of the semiconductor–metal interface induce localized electronic states whose energies lie in the semiconductor band gap. These localized states pin the Fermi level at the energy of the state. The precise nature of the defects responsible for the Fermi level pinning has not yet been determined. Spicer and co-workers[2] suggest that defects associated with missing cation and anion atoms, acting respectively as donor and acceptor levels, are responsible for the pinning. These assignments in the "Unified Defect Model" were based partly on the observation of different pinning positions for n- and p-type material at monolayer coverages. It was argued that acceptor levels are required to pin the Fermi level in n-type material and donor levels are required in p-type material. The difference in the pinning positions was argued to result from the difference in the energy levels of the donor and acceptor defects. The present authors, however, showed[3] that a single vacancy species can behave as both donor and acceptor in III–V semiconductors. The vacancy has three charge states, positive, neutral, and negative and thus can pin the Fermi level in both n- and p-type material. The Fermi level would be pinned at a higher energy in n-type material than in p-type material because of the Coulombic repulsion between electrons in the negative charge stage of the vacancy. In addition, the anion vacancy levels in various III–V semiconductors were shown[3] to have trends consistent with observed Schottky barrier heights.

In this paper we extend the theoretical investigation of vacancy levels to include zinc blende II–VI materials. In particular we compare the case of vacancies in II–VI semiconductors with those in III–V materials. We find that neutral vacancies in the II–VI compounds have an even number of electrons, while in III–V's, they have an odd number. Anion vacancies in the II–VI semiconductors studied are double donors, while cation vacancies produce double acceptors in CdTe and both double acceptors and double donors in ZnTe. This is in contrast to the dual role of single donor and single acceptor that vacancies play in III–V's. We suggest key experiments to test the importance of vacancies in determining the Fermi level pinning positions in II–VI's.

In the III–V semiconductors,[3,4] we distinguish two cases for vacancies that are within two atomic layers of the surface (very near surface vacancies), and vacancies that are further removed from the surface. Vacancies of the latter type are essentially the same as bulk vacancies while the surface produces rather substantial splittings and changes in the electronic levels of the very near surface vacancies. Some information on the electronic states and character of the distortions is available for bulk vacancies. Very little information is available on the surface vacancies. Therefore, we treated[3] distortions and Coulomb effects for the bulk vacancies only.

The results on bulk vacancies may be directly relevant to the surface and interface problem. All vacancies except those within two atomic layers behave as bulk vacancies. Hence, some of the surface related vacancies have bulk properties. Further, the trends in the positions of the electronic levels in the bulk vacancies are preserved in the very near surface vacancies.[3,4]

The paper is organized in the following way: in Sec. II, we briefly describe how the calculations are performed, in Sec. III we describe the charge states of bulk vacancies in III–V and II–VI materials, in Sec. IV we present our results for surface vacancy levels, and in Sec. V we state our conclusions.

II. METHOD OF CALCULATION

We consider vacancies near the (110) surface of III–V and II–VI semiconductors. The calculations were performed using the Koster–Slater approach, with a Hamiltonian of tight-binding form, as described in Ref. 4. The semiconductor surface is described by a finite slab of nine atomic layers. The surface atoms are relaxed. Where possible, the surface geometry determined from LEED results[5] is used; for materials

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TABLE I. Calculated one electron energies of the ideal vacancy measured with respect to the valence band maximum. Spin-orbit interaction is included for CdTe and splits the t_2 level into a twofold level and a higher fourfold level. The highest occupied level in the ideal, neutral vacancy is indicated by a (+).

Material	Calculated band gaps (eV)	Cation vacancy levels (eV)		Anion vacancy levels (eV)	
		a_1	t_2	a_1	t_2
GaAs	1.5	<0	0.45^+	0.05	1.05^+
InAs	0.4	<0	0.25^+	0.05	E_g
AlAs	2.3	<0	0.8^+	0.8	1.6^+
ZnTe	2.5	<0	1.2^+	2.45^+	$>E_g$
CdTe	1.6	<0	$0.05, 0.06^+$	$>E_g$	$>E_g$

for which LEED results are unavailable, we take the geometry proposed in Ref. 6.

The aforementioned calculations yield electron energy levels neglecting lattice relaxation (the Jahn–Teller effect) and Coulomb repulsion among the electrons bound to the vacancy. Without these effects, the various charge states of the vacancy have the same energy. In Ref. 3, we showed how corrections can be made for lattice relaxation and Coulomb repulsion for anion vacancies in the III–V's. The extension to cation vacancies in III–V's and to vacancies in II–VI's is similar and will be detailed in a longer publication.[7] The corrections yield different energies for the various charge states, and hence a series of donor and/or acceptor levels.

III. VACANCIES IN THE BULK

An ideal vacancy (ideal meaning without lattice distortion and Coulomb repulsion) in the bulk of a III–V or II–VI semiconductor induces a twofold degenerate a_1 level and a sixfold degenerate t_2 level. The a_1 level occurs at lower energy than the t_2. Our calculated energies of ideal vacancies in GaAs, InAs, AlAs, ZnTe, and CdTe are arranged in Table I for comparison. For an ideal anion vacancy in a II–VI material, there are two electrons associated with the levels; hence the a_1 level is completely filled (if it is in the gap) and the t_2 is empty. Anion vacancies in III–V semiconductors have three electrons associated with the levels and so the a_1 is filled and the t_2 contains one electron. Neutral cation vacancies in III–V's have five electrons, so that the a_1 is filled and the t_2 has three electrons. In a II–VI mateial the neutral cation vacancy has six electrons so that the a_1 is filled and the t_2 has four electrons.

Two corrections to the case of the ideal vacancy must be considered to obtain realistic results. First, the lattice relaxes around the vacancy. For those cases in which the t_2 level is partially occupied (all except the anion vacancy in the II–VI's), a Jahn–Teller distortion occurs to split the degeneracy of the t_2 level, lowering the total energy. Second, the electrons bound to the vacancy will repel each other, the Coulombic interaction raising the energy. The effects of these corrections are illustrated schematically in Fig. 1.

The degree and character of the lattice distortion is determined by the ocupation of the levels. For all cases, a breathing mode relaxation can occur which does not split the t_2 level. For neutral anion vacancies in II–VI materials, the t_2 level is empty, and so only breathing mode distortions can lower the energy to first order. When the t_2 level is partially occupied, it is energetically favorable for a symmetry-reducing distortion to occur. It is known that the positive vacancy in Si, with three electrons, undergoes tetragonal distortion which splits the t_2 into a twofold and a higher fourfold level, with one electron occupying the twofold level.[8] (The twofold degeneracy is required by time-reversal symmetry and cannot be removed by lattice distortions.) We assume that the neutral anion vacancy in III–V compounds, with three electrons, also undergoes tetragonal distortion, and the resulting degeneracies are pictured in Fig. 1. The negative vacancy in Si has five electrons, causing the fourfold level to be split further by mixed tetragonal and trigonal distortions.[8] We assume that the same type of distortion occurs for the cation vacancy in III-V's, which have five electrons in the neutral state. These vacancies are shown in Fig. 1 with only twofold levels remaining. Finally, the cation vacancies in II–VI's are known to have trigonal distortion when charged singly negative[8] (that is, with seven electrons), and we assume the same distortion holds for the neutral state. The vacancy with eight electrons (doubly charged negative cation vacancies in II–VI's) has no orbital degeneracy and thus only breathing mode distortions lower the energy to first order. The pattern with increasing occupation is thus seen to go from pure breathing mode to tetragonal, to mixed tetragonal and trigonal, to trigonal, and finally to pure breathing.

Specifically, we have calculated the change in energy due to lattice relaxation for anion vacancies in GaAs and AlAs and

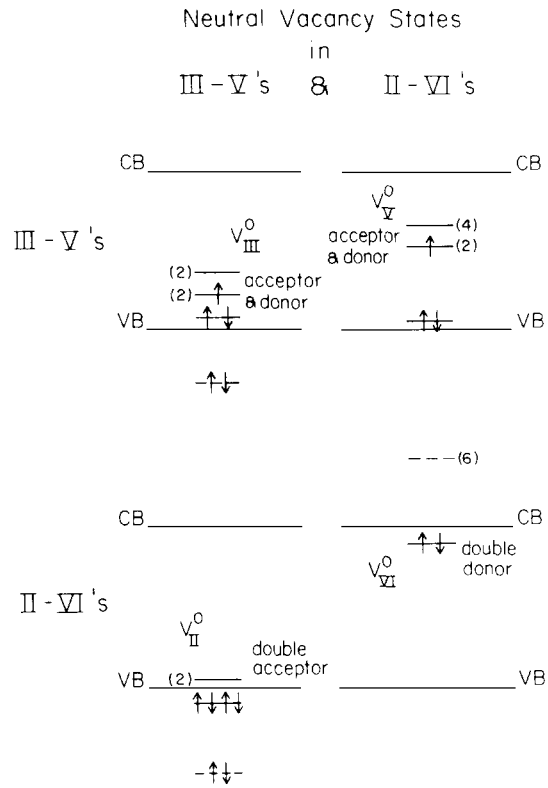

FIG. 1. The electronic states of neutral vacancies in the bulk of III–V and II–VI semiconductors. This schematic picture shows the expected electron occupation (arrows), level splittings, and residual degeneracies of levels (in parentheses).

cation vacancies in CdTe and ZnTe. This was done to first order in the change in the Hamiltonian, as described in Ref. 3, with tetragonal distortion for vacancies with three electrons and trigonal for those with six, as described in the preceding paragraph. Complete details will be published in a longer work,[7] but here we give some of the results. For As vacancies in GaAs and AlAs, the occupied levels are lowered by 0.07 and 0.02 eV, respectively, below the ideal t_2 level. For ZnTe and CdTe, the cation vacancy level is lowered by 0.01 and 0.04 eV, respectively. These relaxations are relative to the ideal vacancy energies of Table I.

An important point to notice in Fig. 1 is that in III–V materials the highest occupied level for both types of vacancies contains one electron. Because this level is partially filled, the vacancies in III–V's can charge with either sign and can behave both as single donors and single acceptors. Changing the occupation changes the lattice distortion. Also, the increased Coulomb repulsion from several electrons bound to the defect will increase the energy. The situation expected for anion vacancies in III–V semiconductors is illustrated schematically in Fig. 2. The lines indicate where the Fermi level would lie at a transition from one charge state to another.[9] We have calculated the splitting between the donor ($V^+ \rightarrow V^0$) and acceptor ($V^0 \rightarrow V^-$) levels for As vacancies in GaAs and AlAs and find it to be 0.05 and 0.2 eV, respectively. The Coulomb repulsion largely determines the splitting, moderated somewhat by lattice distortions. This splitting is in approximate agreement with the observed splitting between the donor and acceptor levels which pin the Fermi level at the surface of GaAs.[1,2]

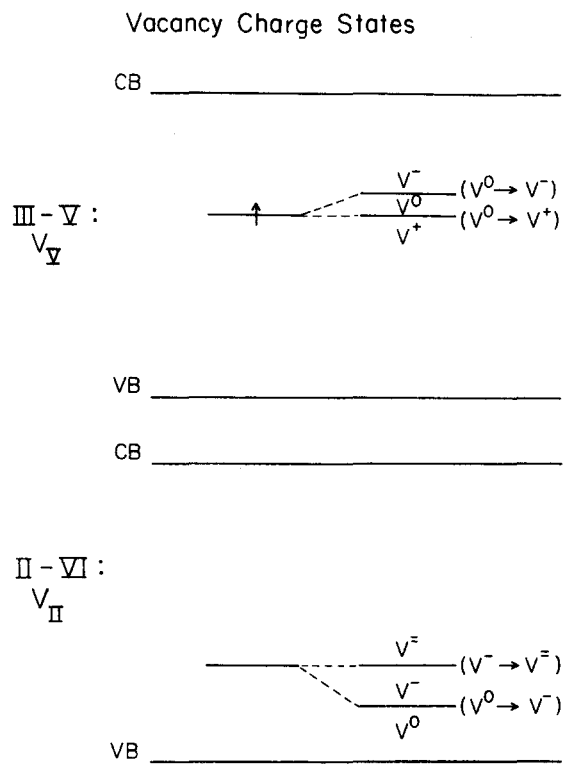

FIG. 2. The effect of Coulomb repulsion on the transition energies for the anion vacancy in a III–V semiconductor and a cation vacancy in a II–VI semiconductor. On the left in each case is the twofold level which is the lowest unoccupied state in the neutral vacancy. The anion vacancy in the III–V compound can gain or lose an electron, while a cation vacancy in the II–VI can gain one or two electrons. The transition energies (Fermi level where the charge changes) is indicated on the right. Coulomb interactions and Jahn–Teller effects split the various charge levels.

By contrast, the highest occupied level of vacancies in II–VI semiconductors (after Jahn–Teller distortion) is filled, as in Fig. 1. The vacancies are charged by removing electrons from a completely filled level, or adding them to a completely empty one. Adding two successive electrons to the empty level produces a double acceptor level, as in Fig. 2. We calculate the levels similarly to what was done for III–V vacancies, only with different distortion, as mentioned. We find that Cd vacancies in CdTe introduce double acceptor levels at 0.05 and 0.07 eV, and that Zn vacancies in ZnTe produce double acceptor levels at 1.2 and 1.4 eV, the doubly charged state existing for Fermi level above the higher energy.

IV. VACANCIES NEAR THE (110) SURFACE

As the vacancy is moved near the (110) surface, there is no significant change in the energy levels until the vacancy reaches the second atomic layer from the surface. At this point a bond with a surface atom is cut. Because of surface relaxation, this hybridization of the surface atoms is different than those in the bulk. Thus, the dangling bonds which form the vacancy bound states occur at different energies when they originate from a surface atom. Any levels of degeneracy greater than two in bulk split into three doubly degenerate levels when the vacancy is on the first or second atomic layer.

In this section we do not take into account the Jahn–Teller effect or Coulomb repulsions. All results presented in this section are for ideal vacancies.[10] The reason for this is that distortions of the lattice around a vacancy on the surface will tend to be large and complicated. Furthermore, while some information on bulk vacancy distortions is available, none is for distortions around surface vacancies.

We first present our results for surface vacancies in III–V materials. We concentrate on the anion vacancies because the bound levels which they produce show trends very similar to measured Schottky barrier heights. In Fig. 3, we show the calculated position of the highest occupied level in the ideal, neutral anion vacancy located in the bulk, in the second atomic layer, and on the (110) surface of $Al_{1-x}Ga_xAs$ and $Ga_{1-x}In_xAs$ as a function of alloy composition. The position of the levels in $Ga_{1-x}In_xAs$, relative to the valence band maximum, is rather independent of the mole fraction x, whereas the levels in $Al_{1-x}Ga_xAs$ show a distinct slope. We also show in Fig. 3 the measured values of the hole barrier of AlGaAs and GaInAs as functions of mole fraction. We note that there is a strong similarity between the calculated positions of the highest filled neutral anion level and the measured hole barrier. We note particularly that as one goes from GaAs to AlAs, the hole barrier increases, and so do the predicted energy levels of an arsenic vacancy. Cation vacancy levels do not show such trends. It is important to point out that the trends observed in ideal anion vacancy calculations reflect the trends in the cation dangling bonds around the vacancy forming the state; any other more complicated defects dominated by cation dangling bonds would have the same trends.

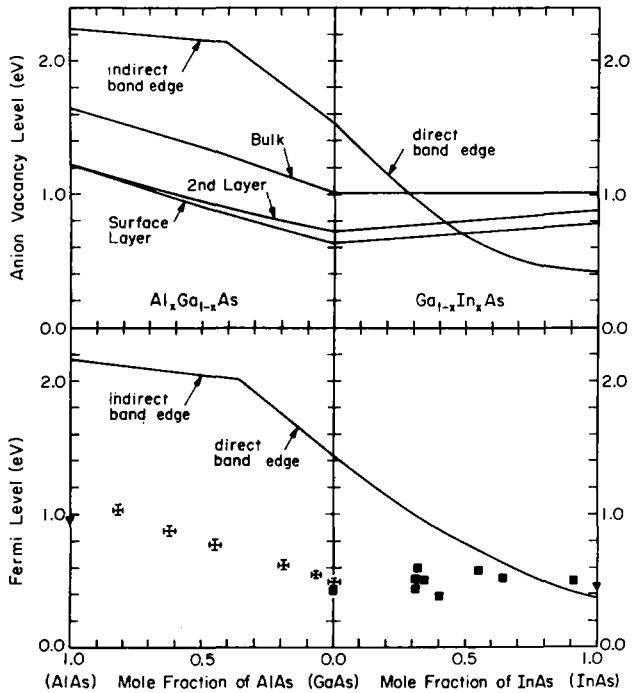

FIG. 3. In the top frames, the calculated position of the highest occupied state of neutral anion vacancies in the bulk, second, and surface layers of $Al_xGa_{1-x}As$ and $Ga_{1-x}In_xAs$ as functions of mole fraction x are presented. The valence band maximum is taken as the energy origin, and the calculated conduction band minima are included. In the bottom frames, the experimental data for hole barriers on the same material are presented. The data represented by crosses are from J. S. Best, Appl. Phys. Lett. 34, 522 (1979). The solid squares and the band gap variation in GaInAs are from K. Kajyama, Y. Mizushima, and S. Sakata, Appl. Phys. Lett. 23, 458 (1973). The inverted triangles are from C.A. Mead, Solid State Electron. 9, 1023 (1966). The measurements of the band gap for GaAlAs were taken from B. Monemar, K. H.Shih, and G. D. Petit J. Appl. Phys. 47, 2604 (1976).

In Fig. 4, we present the results for ideal cation vacancies near the (110) surface of CdTe and ZnTe.[11] The neutral cation vacancy in II–VI semiconductors has six electrons; in the figure the highest occupied levels in the neutral vacancy are marked by arrows. (The energy levels on the fifth layer differs from the levels in Fig. 1 because lattice relaxation is included schematically in the results of Fig. 1.) In particular, the t_2 level of the ideal vacancy at the fifth layer shown in Fig. 4 is in the band gap. Lattice relaxation splits this level and pushes the occupied levels toward the valence band as shown in Fig. 1. For a level structure such as that for the vacancies on the surface layer in Fig. 4, the Fermi level would be pinned at the highest occupied level if a positive charge layer is required and at the lowest empty level if a negative charge layer is required. The cation vacancy levels in CdTe are closer to the valence band than in the more covalent ZnTe, so that these levels do not follow the common anion behavior displayed by InAs and GaAs.

V. CONCLUSION

In the III–V's the simple anion vacancy is capable of accounting for the trends in Fermi level pinning position and the differences observed for p- and n-type material with pre-metallic coverages (coverages of metal atoms which are not thick enough to form a metal). The trends between different III–V materials is characteristic of the cation dangling bonds forming the anion vacancy and would carry over to a large class of defects whose character is dominated by cation dangling bonds. The anion vacancy can act as donor or acceptor (charging with either sign) and so pin the Fermi level in the gap for both p- and n-type materials at pre-metallic coverages.

In the II–VI materials studied here we find that the anion vacancies produce shallow double donors. The cation vacancies produce a deep double acceptor (with possibility of a doubly occupied level slightly above the valence band edge, which we will neglect in the rest of this discussion). The anion vacancy can only charge positive for the Fermi level in the gap. Hence, for pre-metallic coverages it can pin the Fermi level on p-type material. The precise pinning position depends on the charge states involved and on the spatial locations of the defects.

The cation vacancy can only charge negatively for the Fermi level in the gap. Hence, for pre-metallic coverages it can pin the Fermi level on n-type material. Again the precise Fermi level pinning position will depend on the charge states and spatial location of the vacancies involved.

According to Humphreys *et al.*[12] the values of the fully formed Schottky barrier heights on CdTe vary for different surface preparation techniques and experimental method for determining their values. These data are interpreted in terms of reactions between the metal and unstable CdTe surface. Only one set of Schottky barrier measurements have been

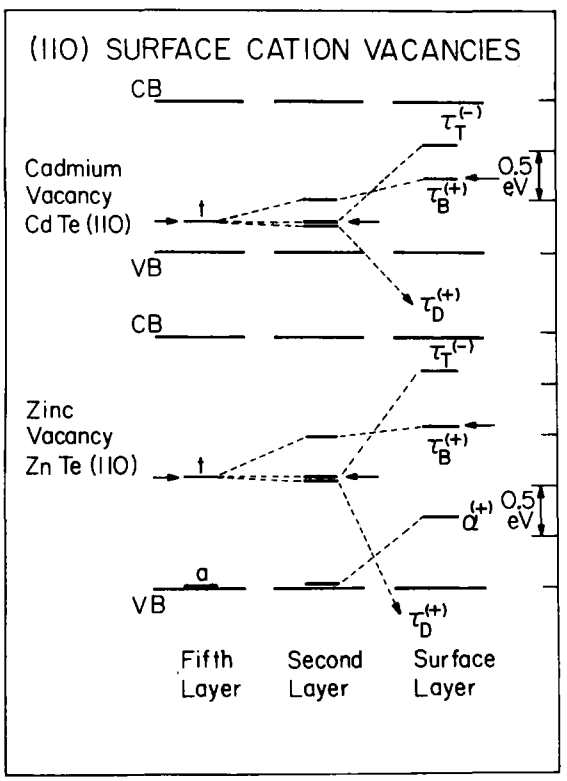

FIG. 4. Energy positions, relative to the band edges, of ideal cation vacancies near the (110) surface of CdTe and ZnTe. The bound state energy levels are essentially the same as those in the bulk until the vacancy reaches the second atomic layer from the surface. The arrows indicate the highest energy state occupied in the neutral vacancy.

reported for ZnTe.[13] Comparing these results with those originally reported by Mead and Spitzer[14] and confirmed by Takebe *et al.*[15] for CdTe, one finds that the barrier height for Au on p-type material is approximately the same for ZnTe and CdTe. Comparing these observations with our results, we note that the pinning position for anion vacancies is too close to the conduction band edge. For cation vacancies, we would not predict a "common anion rule."[16] However, given the rather uncertain experimental situation, it is difficult to conclude whether or not these defects could play an important role in determining the barrier heights on these materials. However, as discussed above, these results do suggest that one test for the importance of vacancies in the II–VI's is to examine the relative Fermi level positions for pre-metallic coverages on n- and p-type materials.

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[1]I. Lindau, P. W. Chye, C. M. Garner, P. Pianetta, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. **15**, 1332 (1978); P. W. Chye, I. Lindau, P. Pianetta, C. M. Garner, C. Y. Su, and W. E. Spicer, Phys. Rev. B **18**, 5545 (1978).

[2]W. E. Spicer, I. Lindau, P. Skeath, and C. Y. Su, J. Vac. Sci. Technol. **17**, 1019 (1980).

[3]M. S. Daw and D. L. Smith, J. Vac. Sci. Technol. **17**, 1028 (1980).

[4]M. S. Daw and D. L. Smith, Phys. Rev. B **20**, 5150 (1979).

[5]LEED geometries are available for GaAs (110), InP (110), ZnTe (110), and GaP (110). See C. B. Duke, R. J. Meyer, and P. Mark, J. Vac. Sci. Technol. **17**, 971 (1980) for the first three, and C. B. Duke, A. Paton, J. Carelli, and A. Kahn (to be published) for GaP. We thank C. B. Duke for sending us a complete set of available geometries.

[6]D. J. Chadi, Phys. Rev. Lett. **41**, 1062 (1978); D. J. Chadi, Phys. Rev. B **19**, 2074 (1979).

[7]M. S. Daw, D. L. Smith, and T. C. McGill (in preparation).

[8]G. D. Watkins, *Proceedings of the 1972 Reading Conference on Radiation Defects in Semiconductors* (Institute of Physics, London, 1973), p. 228.

[9]It is possible that the neutral state is not stable; that is, the vacancy could behave as a "negative-U center". See G. A. Baraff, E. O. Kane, and M. Schluter, Phys. Rev. Lett. **43**, 956 (1979). However, our calculation (see Ref. 3) indicates that the anion vacancy in III–V semiconductors does have a stable neutral state.

[10]By "ideal" we mean that the surface is relaxed according to the LEED data of Ref. 5, but that further distortions around the vacancy are not included.

[11]Our calculations place surface states at the band edges for the (110) surface of ZnTe. A similar situation was found for GaP.

[12]T. P. Humphreys, M. H. Patterson, and R. H. Williams, J. Vac. Sci. Technol. **17**, 886 (1980).

[13]W. D. Baker and A. G. Milnes, J. Appl. Phys. **43**, 5152 (1972).

[14]C. A. Mead and W. G. Spitzer, Phys. Rev. **134**, A713 (1964).

[15]T. Takebe, J. Seraie, and T. Tanaka, Phys. Status Solidi **47**, 123 (1978).

[16]J. O. McCaldin, T. C. McGill, and C. A. Mead, J. Vac. Sci. Technol. **13**, 802 (1976).